

CONTRACT REPORT NO. 15L83-00005

THE OPTIMIZATION OF INJECTION
TECHNOLOGY FOR HIGH
QUALITY STEEL

PHASE I - FINAL REPORT

DESULPHURIZATION OF HOT METAL
WITH CALCIUM CARBIDE

BY

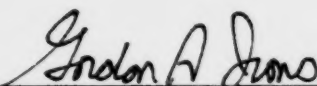
G.A. IRONS, W-K. LU AND L-K. CHIANG
DEPARTMENT OF METALLURGY AND MATERIALS SCIENCE
McMASTER UNIVERSITY
HAMILTON, ONTARIO
L8S 4L7

JANUARY 17, 1985

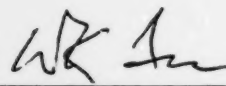
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79 pp

This Final Report is respectfully submitted to Supply and Services Canada and the Physical Metallurgy Research Laboratory of the Ministry of Energy, Mines and Resources under the terms of the Contract "The Optimization of Injection Technology for High Quality Steel - Phase I", 03 SU. 23440-2-9186.



Dr. G.A. Irons
Principal Investigator
Associate Professor



Dr. W-K. Lu
Co-Principal Investigator
Stelco Professor of Metallurgy

Department of Metallurgy and Materials Science
McMaster University
Hamilton, Ontario
L8S 4L7

January 17, 1985

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ACKNOWLEDGEMENTS

The authors would like to acknowledge the contributions of Stelco, Inc. to this project. They permitted us to carry out preliminary trials before this contract started, and donated manpower and equipment during the contract. Without the excellent support and co-operation of Stelco personnel, this project could not have been accomplished. In particular, Messrs. Ian Cameron, Lorne Murphy and Doug Nishizaki provided a great deal of expertise and assistance.

Thanks also go to Cyamamid, Canada Inc. for graciously supplying the special reagents used in these experiments.

Finally, the financial support of the Physical Metallurgy Research Laboratories (PMRL) of the Ministry of Energy, Mines and Resources on the basis of strong recommendations from Stelco, Inc., Algoma Steel Corporation, Dofasco, Inc., and Q.I.T. - Fer et Titane, are all gratefully acknowledged.

1. SUMMARY

Forty-eight successful injections of commercial-grade calcium (DSR) carbide into 2.5 Tonne heats of hot metal were carried out. The most important conditions were the type of top slag, solid to gas loading and oxygen activity. Four slag initial conditions were studied: no slag, a dry top slag (60% CaO, 40% SiO₂), a liquid slag (a commercial continuous casting powder, basicity 1.3) and the dry slag modified by pre-plunging of aluminum. The calcium carbide utilization, fraction of sulphur removed and reaction rate increased in the above order. The solid to gas loadings ranged between 15 and 160 kg/Nm³, and it was found that lower loadings were beneficial to utilization, sulphur removal and reaction rate. Oxygen activity measurements showed that aluminum additions were associated with low oxygen activity and excellent desulphurization results. It is also shown that oxygen was detrimental to the plume reactions and to the top slag reactions.

2. RECOMMENDATIONS

Oxygen was found to play a crucial role in desulphurization, particularly to achieve sulphur levels below 0.005% S. For full-scale trials, deoxidation before carbide injection may be most beneficial. It is also possible that carbide mixed with a deoxidant such as aluminum or magnesium would be beneficial.

On a commercial basis, diamide lime (CaCO_3) is always injected with calcium carbide. The carbon dioxide evolved is an oxidizing gas. Tests should be performed to determine if diamide lime is detrimental for achieving sulphur levels below 0.005% S. Tests should be performed to determine if nitrogen, magnesium and CaCN_2 are suitable replacements for diamide lime to achieve good stirring.

3. INTRODUCTION

Ladle metallurgy operations have proven to be very effective in improving steel quality and reducing production costs. However these processes have been developed in the plant, and consequently the kinetics of the processes are poorly understood and the processes are far from optimum. Fundamental studies at McMaster on powder injection has elucidated the fluid mechanics and heat transfer aspects of these processes with water models, liquid lead models and mathematical models.

Well-controlled injection experiments on ladle metallurgy reactions such as desulphurization have not been carried out. The current experiments were performed at the 3 Tonne scale so that conditions could be accurately measured and controlled. The particular system chosen to work with was calcium carbide desulphurization of carbon-rich iron (hot metal). Currently in Canada, sulphur is the most problematic impurity, and therefore all the integrated steel producers desulphurize their hot metal. From a thermodynamic and cost viewpoint, it is much better to desulphurize hot metal than steel. Calcium carbide was chosen as the reagent because it is used commercially, and because it is probably simpler to understand than the other popular reagent: lime-magnesium mixtures. It is believed that the fundamental understanding of injection processes gained from this system can be applied to other systems.

This project was supported by Energy, Mines and Resources (Physical Metallurgy Research Laboratories) on the recommendations of Stelco, Inc., Algoma Steel Corporation, Dofasco, Inc., and Q.I.T. - Fer et Titane.

The experimental work was carried out at Stelco's Pilot Plant in their Research Centre. Without the excellent support and co-operation of Stelco personnel, this project could not have been accomplished.

The work was aimed at understanding and improving hot metal desulphurization with calcium carbide. The results have focussed on three critical parameters: reagent

efficiency, amount of sulphur removed and reaction rate. A particular plant may want to optimize one of these parameters or some combination. The most important variables which affect these parameters are the condition of the top slag, the injection conditions and the oxygen potential in the system. The present results quantitatively demonstrate these effects. Based on these results, models will be developed which will translate these effects to the full-scale. These models will be useful for analysing the full-scale test results that have been recommended.

4. EQUIPMENT AND PROCEDURE

4.1 POWDER DISPENSER

The present work was carried out on a 3 tonne induction furnace, located at the pilot plant of STELCO Inc. in Burlington, Ontario. A conventional pilot scale powder dispenser was specially modified for the present study. Extensive preliminary trials indicated that the powder feed rate was dependent on the pressure difference across the dispenser, orifice diameter of the outlet valve and the characteristics of the powder. A schematic diagram of the pilot scale dispenser is shown in Figure 1.

During an injection, the powder injection rate was controlled by the difference between the bottom pressure of dispenser and the pipeline pressure directly below the outlet valve of the dispenser. The main carrier gas flow rate was accurately and reproducibly controlled by a needle valve. Only 5 to 10% of the gas flow was found to be going through the dispenser during injection. By properly adjusting the needle valve, the fluctuation of the gas flow rate were minimized so as to maintain constant gas flow rate.

The powder dispenser was equipped with a load cell and mass flow meter for continuous measurement of dispenser weight and total gas flow rate, respectively. Capacitance transducers and pressure transducers were also installed at 2 points in the pipeline for monitoring the instantaneous volume fraction of solids and static pressure.

The gas and powder flow rate, pipeline pressure, and solid volume fraction were recorded 60 times a second with a customized DEC LSI-11/2 computer.

4.2 FURNACE CONFIGURATION

Details of the lance and furnace arrangements are shown in Figure 2. The lance was located at the center of the furnace. The depth of the lance submerged into hot metal was about $650 \text{ mm} \pm 25 \text{ mm}$. The total hot metal weight used for the present study was between 2.2 and 2.6 tonnes.

4.3 MATERIALS

The principle materials used in this study are shown in Table I. Four different initial top slag conditions were used:

- 1) no slag
- 2) a dry slag which was a mechanical mixture of CaO and SiO_2 in a weight ratio of 1.2:1
- 3) a liquid slag which was a commercially available continuous casting powder with the composition shown in Table I, and a liquidus temperature of 1135°C
- 4) the dry slag used above, modified in most cases by the plunging of 4 kg aluminum before calcium carbide injection. This slag appeared liquid. Two injections were performed using a flux (see Table 5) to modify the slag.

These four slag conditions were chosen so as to determine the significance of this variable. Generally 10 kg of top slag was used, and more than 10 kg of calcium carbide was injected so that at the end of injection the slag was solid or semi-solid.

The calcium carbide was a commercial desulphurizing reagent (DSR) as shown in Table I. Note that no diamide lime (CaCO_3) was used for most of the runs.

4.4 PROCEDURE

The detailed experimental procedure is shown in Figure 3. At the beginning of injection test, the initial sulphur content of the iron was adjusted to the desired level by plunging a box containing sulphur into the bath. The temperature was controlled to $1350^\circ\text{C} \pm 5^\circ\text{C}$.

Before a number of the injection test, the oxygen potential and hot metal temperature were measured simultaneously by CELOX2/CLL type oxygen probe. A pair of slag and metal samples was taken before the start of injection. The injection lasted between 1 and 6 minutes. This was dependent on the rate of solid injection. One or two minutes of Ar-gas bubbling was conducted after the CaC_2 injection for the purpose of the metal/slag reaction studies. During

the injection and Ar-gas bubbling treatment, hot metal samples were taken every 15 to 20 seconds to obtain detailed information on the change of sulphur during treatment of hot metal. After the injection and bubbling treatment, the oxygen potential and bath temperature were measured. A pair of slag and metal samples was also taken as a measure of the final slag and metal chemistry. The top slag was then thoroughly skimmed off the furnace. The furnace was covered by a lid during the treatment.

4.5 OPERATING CONDITIONS

The ranges of injection conditions are shown in Table II and a loading diagram for all the runs is shown in Figure 4.

TABLE I
COMPOSITION OF MATERIALS

Hot Metal	C 3.5% ~ 4.0%	Mn ~ 0.5%	(1350 ± 5°C)
	Si 0.2% ~ 0.5%	P 0.040 ~ 0.045%	
Initial Top Slag	No Slag		
	Dry Slag	CaO/SiO ₂ = 1.2	
	Liquid Slag	Continuous Casting Powder ¹	
	Modified Slag	Dry Slag + Aluminum	
Powder Injected	DSR ²	Particle Size ~ 30 μm	
Flux	CaO 45%, CaF ₂ 20%, Al 30%, C 5%		
Carrier Gas	Argon, commercial grade		

1. 1/STG c.c. powder

CaO 31.5 ~ 33.5%, SiO₂ 25 - 27%, Al₂O₃ 6.5 ~ 7.5%

MnO 5 ~ 6%, Na₂O 6.5 ~ 7.5%, Tot.C 6.5 ~ 7.5%

F 5.5 ~ 6.5%

CaO/SiO₂ = 1.30

Melting Temp. 1135°C

2. DSR

CaC₂ 81%, CaO 10.6%, CaS 0.9%

C 0.5%, MgO 0.3%, ASH 6.3%

TABLE II
RANGES OF OPERATING CONDITIONS

Powder consumption (kg/t)	1.3 ~ 7.6
Powder injection rate (kg/min)	2.5 ~ 11.0
Gas flow rate (Nm ³ /min)	0.05 ~ 0.24
Solid/Gas Ratio (Loading)	16 ~ 154
Treating Injection + Bubbling (min)	2.5 ~ 6.0

5. RESULTS AND DISCUSSION

Forty-eight successful injection tests were carried out. The injection tests were divided into four groups according to the initial slag conditions; namely no slag, dry slag, liquid slag, and modified dry slag.

The injections with no top slag were performed in the summer of 1982, before this contract started. The control of the system was not as good as in the subsequent tests, but they are reported for the sake of comparison. Several other aspects were briefly examined in the 1982 injections. Both DSR and CAD commercial grade calcium carbide containing diamide lime (CaCO_3) were used. An attempt was also made to use the co-injection technique; in the later stage of the injection, salt-coated magnesium was simultaneously injected from a separate dispenser. The co-injection period was 20 to 30 seconds. The injection rate of salt-coated magnesium was between 0.85 and 3.0 kg/min. The operating conditions and results are shown in Table III, and Appendix I.

For the contract, thirty-seven successful injection tests, with initial slag conditions of dry slag, liquid slag, and modified dry slag, were performed under very accurate control of the injection conditions. The desulphurizer used in 35 of the injection tests was DSR grade commercial carbide with a particle size of 30 μm . Two injection tests were also done with a coarser particle size (300 μm). Details of slag conditions, operating conditions, and changes in sulphur content are shown in Table III.

The discussion of these results is divided into three sections:

- <1> The effect of top slag.
- <2> The effect of injection conditions.
- <3> The effect of oxygen potential.

TABLE III. SUMMARY OF RESULTS

INJECTION	DATE DA-MO-YR	TOP-SLAG		CaC ₂ (DSB)		ADDITIONS (kg)	ARGON RATE (Nm ³ /min)	SULPHUR CONTENT (%)			OXYGEN PROBE (mV)	
		TYPE	QUANTITY (kg)	RATE (kg/min)	QUANTITY (kg)			INITIAL	AFTER INJECTION	POST- BUBBLING	BEFORE	AFTER
H1R1	26-04-82	NONE	—	8.41 ¹	20.6 ¹	1.02 Mg ²	0.25 ³	0.075	—	0.006	—	—
H1R2	26-04-82	NONE	—	7.99	9.85	0.283 Mg ²	0.25 ³	0.033	—	0.004	—	—
H1R3	26-04-82	NONE	—	5.10	4.50	—	0.25 ³	0.042	—	0.023	—	—
H1R2	03-05-82	NONE	—	7.76	16.0	—	0.25 ³	0.046	—	0.012	—	—
H2R3	03-05-82	NONE	—	4.83	14.7	1.47 Mg ²	0.25 ³	0.050	—	0.008	—	—
H3R1	12-05-82	NONE	—	7.14 ¹	17.9 ¹	—	0.25 ³	0.064	—	0.014	—	—
H3R2	12-05-82	NONE	—	6.04	16.9	—	0.25 ³	0.057	—	0.005	—	—
H3R3	12-05-82	NONE	—	6.05 ¹	11.2 ¹	—	0.25 ³	0.104	—	0.019	—	—
H3R4	12-05-82	NONE	—	7.17 ¹	10.0 ¹	—	0.25 ³	0.118	—	0.062	—	—
H4R1	17-05-82	DRY	9	6.70 ¹	13.6 ¹	0.45 Mg ²	0.25 ³	0.079	—	0.020	—	—
H4R2	17-05-82	DRY	4	5.6	14.9	—	0.25 ³	0.068	—	0.013	—	—
H5R1	06-03-84	DRY	10	—	—	—	—	—	—	—	—	—
H5R2	06-03-84	DRY	10	2.66	4.65	—	0.164	0.118	0.093	0.083	-40	-42
H5R3	06-03-84	DRY	10	—	—	—	—	—	—	—	-38	-40
H6R1	13-03-84	DRY	10	10.0	16.5	—	0.155	0.082	—	0.007	-42	—
H6R2	13-03-84	DRY	10	5.71	3.82	—	0.155	0.084	0.077	0.073	—	—
H6R3	13-03-84	DRY	10	7.32	17.9	—	0.168	0.070	0.062	0.002	—	-52
H7R1	20-03-84	DRY	10	6.38	14.4	—	0.240	0.082	0.007	0.000	-46	-54
H7R2	20-03-84	DRY	10	5.14	15.0	—	0.118	0.059	0.003	0.003	-54	-60
H7R3	20-03-84	LIQUID	10	9.49	14.9	—	0.127	0.071	0.013	0.005	-50	-56
H7R4	20-03-84	LIQUID	10	4.02	13.4	—	0.168	0.049	0.006	0.002	-50	-72

TABLE III - SUMMARY OF RESULTS

INJECTION	DATE DA-MO-YR	TOP SLAG		CaO (DSR)		ADDITIONS (kg)	ARGON RATE (Nm ³ /min)	SULPHUR CONTENT (%)				OXYGEN PROBE (mV)	
		TYPE	QUANTITY (kg)	RATE (kg/min)	QUANTITY (kg)			INITIAL	AFTER INJECTION	PAST BUBBLING		BEFORE	AFTER
H0R1	11-07-84	LIQUID	10	2.46	8.23	—	0.125	0.0981	0.066	0.051		-54	-42
H0R2	11-07-84	LIQUID	10	—	—	—	—	—	—	—		-52	-57
H0R3	11-07-84	LIQUID	10	9.12	14.8	—	0.167	0.111	0.059	0.026		—	—
H0R4	11-07-84	LIQUID	10	8.57	11.9	—	0.227	0.051	0.022	0.012		—	—
H0R1	18-07-84	DRY	10	10.7	12.7	—	0.162	0.092	0.063	0.036		-48	-58
H0R2	18-07-84	LIQUID	10	7.1	12.7	—	0.126	0.074	0.039	0.020		-57	-58
H0R3	18-07-84	LIQUID	10	6.57	12.7	—	0.165	0.067	0.022	0.017		-54	-60
H0R4	18-07-84	LIQUID	10	6.90	13.0	—	0.218	0.068	0.022	0.013		-52	-60
H10R1	25-07-84	DRY	10	5.01	12.8	—	0.082	0.092	0.046	0.033		—	—
H10R2	25-07-84	DRY	10	5.15	12.8	—	0.060	0.076	0.056	0.043		-54	-62
H10R3	25-07-84	DRY	10	9.24	12.9	—	0.067	0.094	0.063	0.054		-50	-56
H10R4	25-07-84	DRY	10	3.67	12.8	—	0.060	0.059	0.028	0.021		-54	-58
H11R1	02-08-84	LIQUID	10	5.72	11.8	—	0.078	0.103	0.076	0.047		-56	-62
H11R2	02-08-84	LIQUID	10	6.02	13.2	—	0.049	0.086	0.052	0.035		-58	-58
H11R4	02-08-84	LIQUID	10	1.56	8.12	—	0.051	0.068	0.015	0.012		-56	-62
H11R5	02-08-84	LIQUID	10	2.71	11.0	—	0.049	0.055	0.018	0.016		-62	—
H12R1	08-08-84	LIQUID	20	4.55	11.6	—	0.120	0.097	0.067	0.060		—	—
H12R2	08-08-84	LIQUID	30	4.73	11.5	—	0.125	—	0.079	0.018		-62	—
H12R3	08-08-84	DRY	10	5.916	11.8	—	0.162	0.070	0.034	0.029		-62	-68
H12R4	08-08-84	DRY	10	2.665	11.6	—	0.049	0.070	0.035	0.030		-64	-68

TABLE III - SUMMARY OF RESULTS

INJECTION	DATE DA-MO-YR	TOP SLAG		C (wt% DSR)		ADDITIONS (kg)	ARGON RATE (Nm ³ /min)	SULPHUR CONTENT (%)			OXYGEN PROBE (mv)	
		TYPE	QUANTITY (kg)	RATE (kg/min)	QUANTITY (kg)			INITIAL	AFTER INJECTION	POST H. BRILING	BEFORE	AFTER
H13R1	18-09-84	DRY	10	2.86	10.7	—	0.220	0.096	—	0.021	-60	-66
H13R2	18-09-84	DRY	10	3.76	11.8	—	0.060	0.090	—	0.014	-56	-55
H13R3	18-09-84	DRY	10	— ₅	—	—	—	0.081	—	0.051	-66	-74
H13R4	18-09-84	DRY	10	— ₅	—	—	—	—	—	—	—	—
H14R1	26-09-84	DRY	10	2.86	12.4	4.5 Al	0.160	0.085	0.006	0.003	-190	-168
H14R2	26-09-84	DRY	10	6.94	12.5	4.5 Al	0.162	0.086	—	0.015	-210	-170
H14R3	26-09-84	DRY	10	— ₅	—	4.5 Al	—	0.073	—	0.041	-206	—
H14R4	26-09-84	DRY	10	9.84	13.0	4.5 Al	0.155	0.076	—	0.009	-186	-168
H15R1	04-10-84	DRY	10	3.71	6.62	—	0.161	0.040	—	0.014	-76	-102
H15R2	04-10-84	DRY	10	— ₅	— ₅	4.5 Al	—	0.021	—	0.020	-195	-186
H15R3	04-10-84	DRY	10	7.77	13.0	4.5 Al	0.169	0.018	—	0.003	-170	-120
H15R4	04-10-84	DRY	10	9.72	13.0	4.5 Al	0.080	0.055	—	0.016	-180	-180
H16R3	11-10-84	DRY	20	6.73	12.1	4.5 Al + 5.4 Flux	0.162	0.083	—	0.001	-152	-200
H16R4	11-10-84	DRY	10	3.10	5.1	4.5 Al 7.3 Flux	0.120	0.062	0.024	—	-156	-194

1. CAD (60% DSR + 40% CaCO₃) used instead of DSR.
2. Salt-coated magnesium co-injected at the end of DSR injection.
3. Estimated, between 0.2 and 0.3 Nm³/min.
4. Unsuccessful injection
5. Computer malfunction.
6. DSR 300 µm average particle size instead of 30 µm.

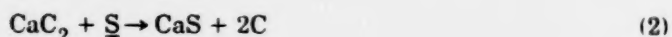
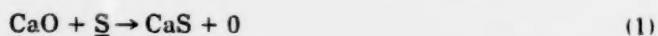
5.1 THE EFFECT OF TOP SLAG

The typical curves of sulphur change with time during the treatment are shown in Figures 5 and 6. These 4 injections were selected because the starting sulphur, gas flow rate and solids flow rate were very similar; the only major difference was the top slag. A significant difference was found between the no slag and dry slag cases on one hand, and the liquid slag, and modified dry slag, on the other hand. The amount of initial slag used in most of injection tests was about 10 kg. For the no slag or dry slag case, a 30 to 50 second "incubation period" is observed initially, Figure 5. The incubation period with no slag was found to be longer than that of the dry slag, 40 sec to 50 sec and 30 sec to 40 sec, respectively. Consequently, this incubation time resulted in low efficiencies of carbide utilization and slow desulphurization.

The sulphur curves with either the liquid slag or modified dry slag exhibited no incubation period as seen in Figure 6. A survey of all the sulphur versus time curves in Appendix I shows that this observation is true for all the injections.

5.1A Reagent Efficiency

In order to calculate the efficiencies of reagent utilization, the stoichiometric equations for desulphurization with calcium carbide and lime in the DSR mixture were used:



Thus if the drop in sulphur content from the initial value (% S_i) to the final value after post-bubbling (% S_b) corresponded to that expected from the total amount of CaC_2 and CaO injected and reacted according to equations 1 and 2, the desulphurization efficiency would be 100%. The DSR reagent used was nominally 81% CaC_2 and 10.6% CaO , thus the ratio of desulphurization from each component would be expected to be similar for all injections. The desulphurizing capability of the top slag itself was not considered in these efficiency

calculations, because the amounts of desulphurization during post-bubbling with top slags was much smaller than those during injection.

Figures 7 to 10 show these efficiencies of desulphurization plotted as a function of initial sulphur content. For the no top slag case, Figure 7, one can see that the efficiency increases with sulphur content. The efficiencies are progressively improved by moving to dry slags (Figure 8), liquid slags (Figure 9) and finally dry slags modified with aluminum (Figure 10). The efficiency also depends on loading (L) and this will be discussed in Section 5.2.

5.1B Degree of Sulphur Removal

The degree of sulphur removal was simply the fraction of sulphur removed:

$$\frac{\%S_i - \%S_b}{\%S_i} \times 100\% \quad (3)$$

These quantities are plotted as a function of kg of DSR added per tonne of hot metal for the four different slag conditions in Figures 11 to 14. One sees that the fraction of sulphur removed increases with the amount of addition, and improves progressively through the four different top slag conditions. (The sulphur removed is also dependent on the loading (L) as described in Section 5.2.) In fact, for the aluminum-modified dry slags the efficiencies were well over 95% corresponding to sulphur levels of 0.001 to 0.003% S.

5.1C Rate of Sulphur Removal

In order to develop a useful index for the rate of desulphurization, it was arbitrarily decided to use

$$\log_e \left(\frac{\%S_i}{\%S_b} \right) \times \frac{1}{\text{injection time}} \quad (4)$$

Strictly speaking, this expression can be applied only to kinetic processes which are first order with respect to sulphur content. Clearly, many of the present results are not first order (i.e.

the results with incubation periods). However the index is useful because it is very high for injections which quickly reached very low sulphurs from high sulphur levels.

This index is plotted as a function of the powder injection rate for the three different top slag conditions in Figures 15 to 17. Once again one sees that there is a small, but progressive improvement in rate in moving from a dry slag to a liquid slag and finally to the aluminum-modified dry slag. The loadings also significantly affect the rate as discussed in Section 5.2.

5.1D Explanation of Top Slag Effects

The phenomenon of the 'incubation period' can be explained as sulphur reversal from top slags with poor desulphurizing properties, or the inability to physically hold the reacted CaS particles.

The initial top slag compositions all drastically change during injection because the initial weight was 10 kg and the carbide additions were generally greater than 10 kg. The carbide in the top slag will be a mixture of unreacted carbide, calcium sulphide from desulphurization in the plume and calcium oxide produced by carbide oxidation. With the dry slag or no slag conditions, the initial CaS rising to the top slag cannot be dissolved in the top slag because it is solid. Therefore the CaS will be exposed to the surface oxygen potential and revert to the metal. Later on (30 - 50 seconds later) the unreacted carbide in the top slag will be sufficient in quantity to hold the CaS away from the slag-metal interface. Therefore the reversion will stop and the incubation period will be over. On the other hand the liquid slag and the modified dry slag have the ability to immediately dissolve the initial quantity of CaS.

The dry slags modified by aluminum addition were found to be very good for improving the reaction rate and reagent efficiency. This is partially due to deoxidation of the hot metal to a low level. (The oxygen potentials are more fully discussed later.) The aluminum addition to slags containing lime is particularly effective because of the formation of molten calcium aluminate:



Therefore this modified slag can immediately dissolve the CaS from the plume reactions.

The effect of slag flux agent and slag volume on the hot metal desulphurization were also studied, and found to be effective in improving slag properties. Again this can be explained by the formation of liquid slags which can dissolve CaS.

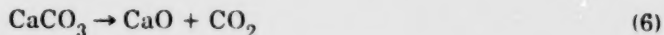
The results indicate that the liquid slags are dramatically better than dry slags in terms of efficiencies and degree of desulphurization. However the overall rate of sulphur removal was only slightly better for the liquid slags. It was found that the dry slag was poor in the rate of sulphur removal initially, but becomes powerful after passing through the incubation period. The dry slag can physically hold and separate the CaS on the CaC_2 particles from contacting the hot metal. Furthermore, most of the carbide travels through the metal plume and is caught in the top slag. Therefore it still possesses some desulphurizing capacity. The refining capacity of CaC_2 -saturated top slag after injection is dependent on its physical properties, basicity, and the extent of unreacted CaC_2 . Under the same gas flow rate, the top slag refining capacity during post bubbling was found to be proportional to the CaC_2 injection rate. This is because a high solid injection rate will cause low efficiencies CaC_2 utilization in the plume due to poor mixing and circulation. (This is discussed in the next section.) Thus, a greater portion of the unreacted CaC_2 powder is expected to mix with the top slag and promote better top slag desulphurization which will continue into the post-bubbling period.

5.2 THE EFFECT OF INJECTION CONDITIONS

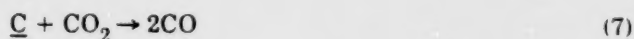
As was mentioned in the previous section, the loading has a significant impact on the efficiency of desulphurization, fraction of sulphur removed and desulphurization rate. The loading parameter used in the study L , is the solids feed rate (kg/min) divided by the carrier gas flow rate at normal conditions (Nm^3/min), thus L is solid to gas ratio in kg/Nm^3 .

One can see that in Figures 8 to 10 for efficiency, Figures 12 to 14 for fraction of sulphur removed and Figures 15 to 17 for desulphurization rate that lower loadings improves the results regardless of the top slag condition. Therefore for comparable solid addition amounts and rates, more carrier gas has a beneficial effect. The reason for this is that the gas flow rate controls the rate of liquid recirculation in the furnace. The liquid recirculation pumps fresh sulphur-rich liquid into the plume zone where reaction occurs, thus the liquid recirculation rate must be matched to the rate of solid addition. In the present experiments enough solids were added to the furnace to theoretically desulphurize the metal in one or two minutes, therefore the rate at which liquid is brought into the reaction zone is crucial for high efficiencies and rates.

On the industrial scale, the situation is somewhat different because diamide lime (commercial CaCO_3) is added with the carbide. The calcium carbonate decomposes to release CO_2 at approximately 900°C according to:



and the CO_2 may subsequently react with carbon dissolved in the hot metal or carbon present in the commercial mixtures to generate even more gas:



These mixtures are generally conveyed to the ladle at as high loadings as possible, because the gas for mixing is released in-situ. In a typical case 60% DSR/40% diamide lime (CaCO_3) is conveyed at loadings L of 200 kg/Nm^3 . However if one assumes that all the carbonate decomposes and the carbon dioxide is converted to carbon monoxide at 1350°C , the loading in the ladle will be approximately 0.75 kg/m^3 . In the present experiments, the argon carrier gas would expand to yield loadings in the ladle of 2.75 kg/m^3 at the lowest (from Figure 4).

Furthermore, most of the carbide injected on an industrial is into torpedo cars. It is known that the mixing is much slower in this configuration compared to ladles such as in the present study⁽¹⁾. Therefore more stirring is required in these situations.

5.3 THE EFFECT OF OXYGEN

As Table III indicates oxygen probe readings were taken before and after most of the heats. For the heats with no aluminum addition the emf values show a slight downward trend at approximately -50 mV due to the injection as Figure 18 shows.

For the heats (H14 and H15, Figures 19 and 20), in which aluminum was used, one can see that the aluminum plunging lowers the emf to between -150 and -200 mV. In general each reading would be higher than the preceding one. Immediately after carbide injection it rises to between 100 and 150 mV. The next aluminum addition; in preparation for the next injection would depress the emf values again. Clearly, the aluminum reduces the dissolved oxygen in the melt.

The correlation suggested by the probe manufacturer to determine the dissolved oxygen is:

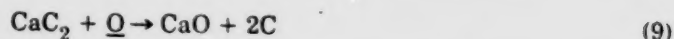
$$\log Q = 1.36 + 0.059 [\text{mV} + 0.3(T - 2822^\circ\text{F}) + 0.00011(T - 2822^\circ\text{F})] \quad (8)$$

This was determined for steelmaking conditions so it should be used cautiously here. Thus -50 and -200 mV correspond to 2.7 and 0.35 ppm Q , respectively. The former value is quite close to silica saturation with the silicon in the hot metal, which is expected to control oxygen at such low temperatures. In theory the oxygen potential after such large additions of aluminum should be below 10^{-3} ppm. However in such an open system, oxygen can come from the atmosphere, slag or refractory. Therefore the instantaneous oxygen reading is just the balance point between the rate at which oxygen is entering the metal and the rate at which it is being consumed by dissolved aluminum. This is consistent with the fact that the oxygen readings drifted upward during the holding periods.

The results presented earlier show that the best results were obtained with the aluminum additions to the dry slag. Therefore the role of oxygen must be carefully considered.

5.3A Plume Reactions

Oxygen can also compete for calcium carbide according to:

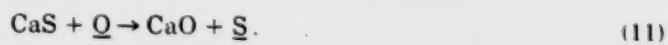


and in fact this reaction is more favored than the desired desulphurization reaction:



The free energy of formation of these two reactions is plotted as a function of oxygen activity for equation (9) and sulphur activity for equation (10) in Figure 21. One can see that at equal oxygen and sulphur activities the oxidation is more favored. Therefore for desulphurization to occur, there must be a much larger amount of sulphur present, given by the horizontal gap between the two lines. At 1350°C, the temperature of the present experiments the ratio between sulphur and oxygen activities must be at least 90 for desulphurization to occur. This ratio becomes smaller for higher temperatures as Figure 22 indicates.

Using the 2.7 and 0.35 ppm $\underline{\text{O}}$ activity calculated above, one would predict on a thermodynamic basis that the lowest sulphur levels attainable would be 0.009 and 0.001% S (assuming that the sulphur activity coefficient is 2.7). In fact, sulphur levels below these values were obtained. This could be due to errors in the oxygen activity measurements, but it could also be due to kinetic factors. In the plume during injection, the oxygen may be much lower than measured after injection due to reaction 9. This permits the desulphurization to proceed further. After injection, the reversion of sulphur may be restricted by slow transfer from the top slag, and the fact the quantities of oxygen present are only in the ppm range so that only a few ppm of sulphur can revert according to

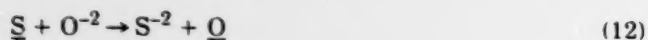


Therefore reducing the flux of oxygen into the system is crucial for good desulphurization results. Even though the measured oxygen levels can be low (a few ppm), this does not mean that oxygen is not entering the system, it means oxygen is being eliminated just as quickly. The elimination is therefore at the expense of silicon or carbon in the hot metal or the desulphurizing reagent or the deoxidizing agent added.

5.3B Top Slag Reactions

The dry top slags processed negligible desulphurizing capacity, however as the injection progressed there would be increasing amounts of calcium carbide in the slag. This carbide could continue to react with sulphur at the slag-metal interface and with sulphur in iron droplets entrained into the slag. As discussed above, these reactions will be stopped by large oxygen activities and fluxes of oxygen.

The liquid slags or dry slags modified by aluminum which became liquid can be analysed by conventional slag-metal thermodynamics. The usual electrochemical reaction mechanism is



where the ionic species are in the slag. Thus high oxygen activity will push the reaction to the left. The sulphur partition coefficient between slag and metal can be obtained from the literature^(2,3). Figure 23 shows the dependence of the sulphur partition coefficient for the liquid slag in present study at 1350°C. The basicity is defined as

$$R_s = \frac{\% \text{CaO} + 0.693\% \text{MgO}}{0.927\% \text{SiO}_2 + 0.184\% \text{Al}_2\text{O}_3} \quad (13)$$

One sees that there is a dramatic change in the partition ratio in moving from 2.7 ppm oxygen activity to 0.35 ppm. Therefore the deoxidized slag can contain much more sulphur.

In summary reduced oxygen activity is beneficial for both the plume reactor and the top slag reactor, so that both are working effectively together.

On an industrial scale diamide lime is always injected with calcium carbide. As mentioned above CO_2 is generated which may be reduced to CO by carbon in the melt. In fact, CO_2 is a very oxidizing gas which may also react with carbide and aluminum to reduce efficiencies. It may also keep the oxygen activity in the melt so high that low sulphur contents ($< 0.01\% \text{ S}$) cannot be achieved. Alternative stirring agents such as nitrogen, calcium cyanamid and magnesium could be evaluated.

6. WORKSHOP ON HOT METAL DESULPHURIZATION

On November 22, 1984, a Workshop on Hot Metal Desulphurization was held at McMaster University to discuss these pilot plant results and to assess the implications for industrial practice. Representatives of Stelco, Inc., Algoma Steel Corporation, Cyanamid Canada, Inc. and CANMET were present.

The representatives of the two steel companies were most interested in the techniques for obtaining sulphur levels below 0.005% which is becoming a common specification immediately after hot metal treatment. Current practice with carbide ($\text{CaC}_2/\text{CaCO}_3$ mixtures with no aluminum) requires large injections and is too inconsistent. The treatment with aluminum (either before or during carbide injection) and the elimination of CaCO_3 from the mixture were discussed, and found worthy of further full-scale experimentation. Cyanamid, Inc., a supplier of calcium carbide, was receptive to improvements in carbide technology. Such full-scale tests can determine if aluminum additions can economically substitute for calcium carbide to consistently achieve low sulphur contents.

It is believed that the Workshop was beneficial to all parties; some of the ideas and comments expressed have been incorporated in this report.

7. FUTURE WORK

Mr. L-K. Chiang will continue analysis of this experimental work for his Ph.D. Thesis. He will develop a mathematical model of the plume and top slag reactions. The fluid dynamics of the plume has already been developed⁽⁴⁾. The modelling will further quantify the discussion presented in this report. Copies of the thesis will be distributed.

A proposal for Phase II of this project will be submitted before the expiry of the Contract, March 31, 1985.

8. REFERENCES

1. Haida, O. and Brimacombe, J.K., Proceedings of SCANINJECT III, 1983, Lulea, Sweden, pp. 5:1 to 5:17.
2. Venkatradi, A.S. and Bell, H.B., J.I.S.I. (1969), pp. 1110-1113.
3. Tamura, K., Ono, K. and Nishida, N., Tetsu-to-Hagame (1981), vol. 67, pp. 2635-2644.
4. Farias, L.R. and Irons, G.A. (1984), submitted to Met. Trans. B.

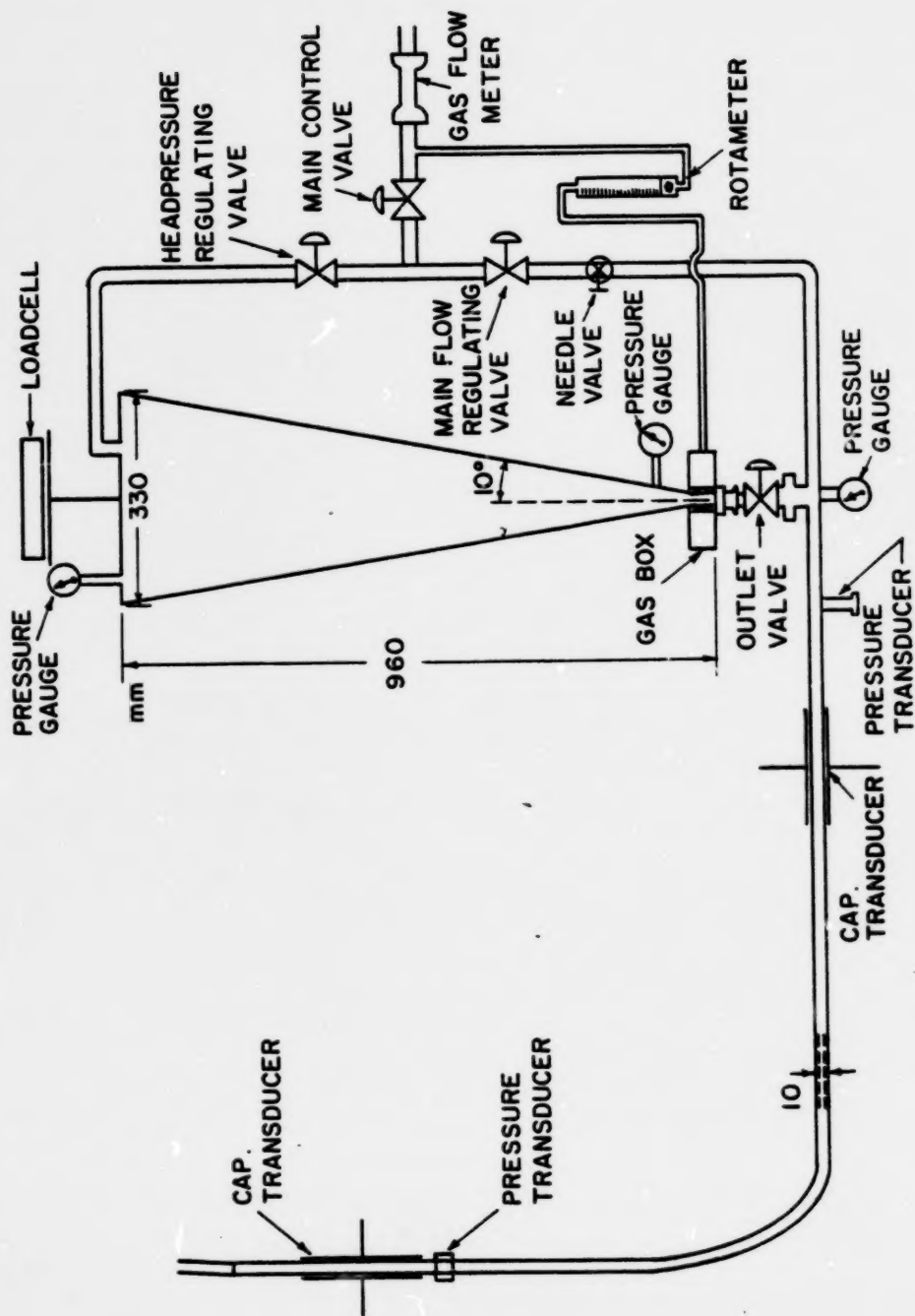


Figure 1: Schematic diagram of power dispenser and conveying line.

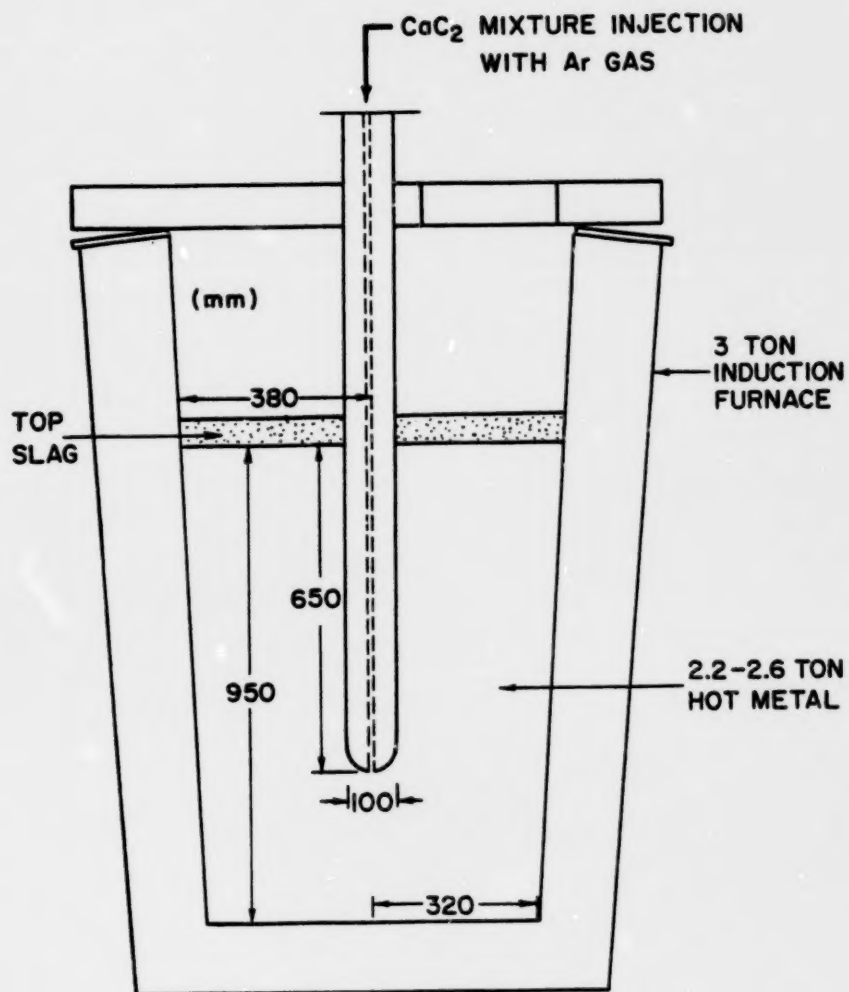


Figure 2: Cross-section showing lance, furnace and metal levels, to scale.

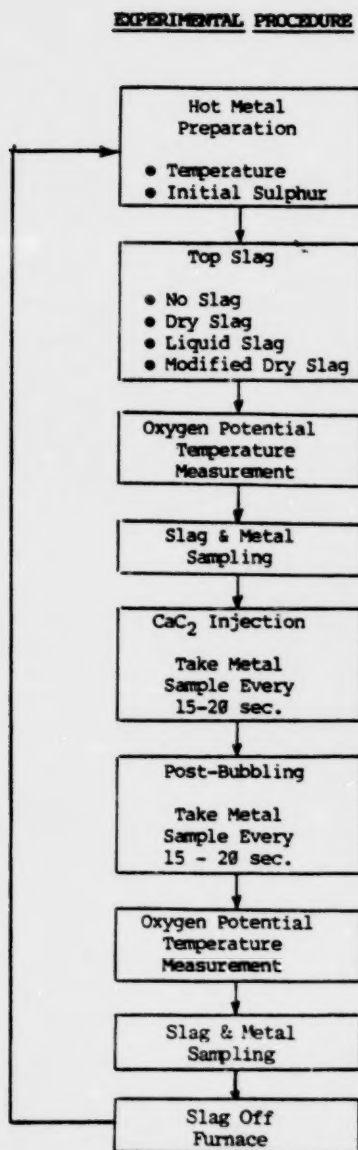


Figure 3: Flowchart for experimental procedure during a heat.

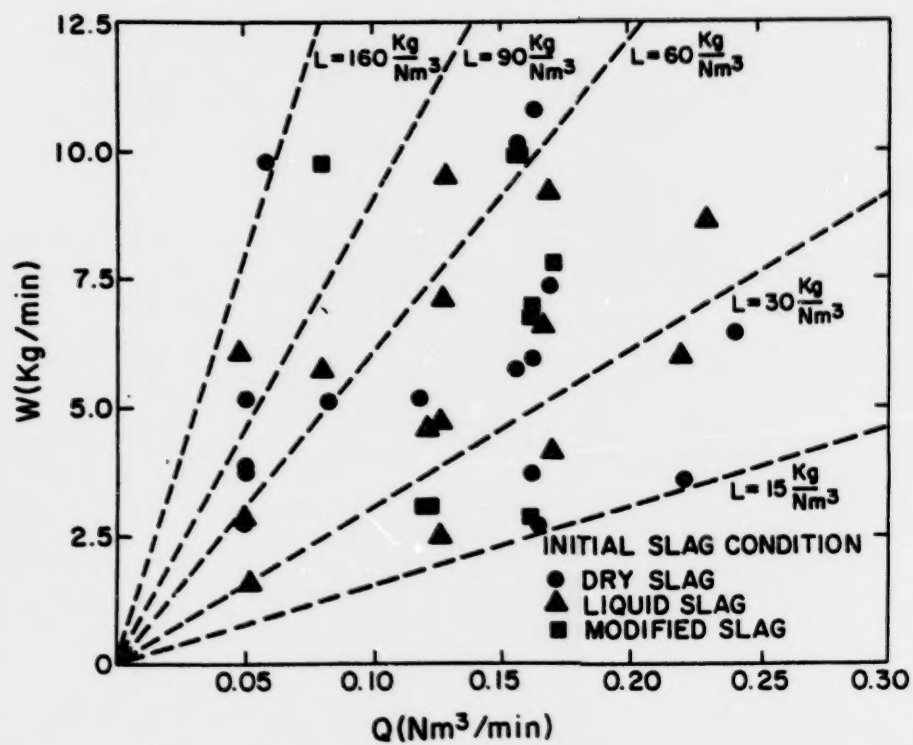


Figure 4: Loading diagram for the injections; W is the solids feedrate and Q is the gas flow rate.

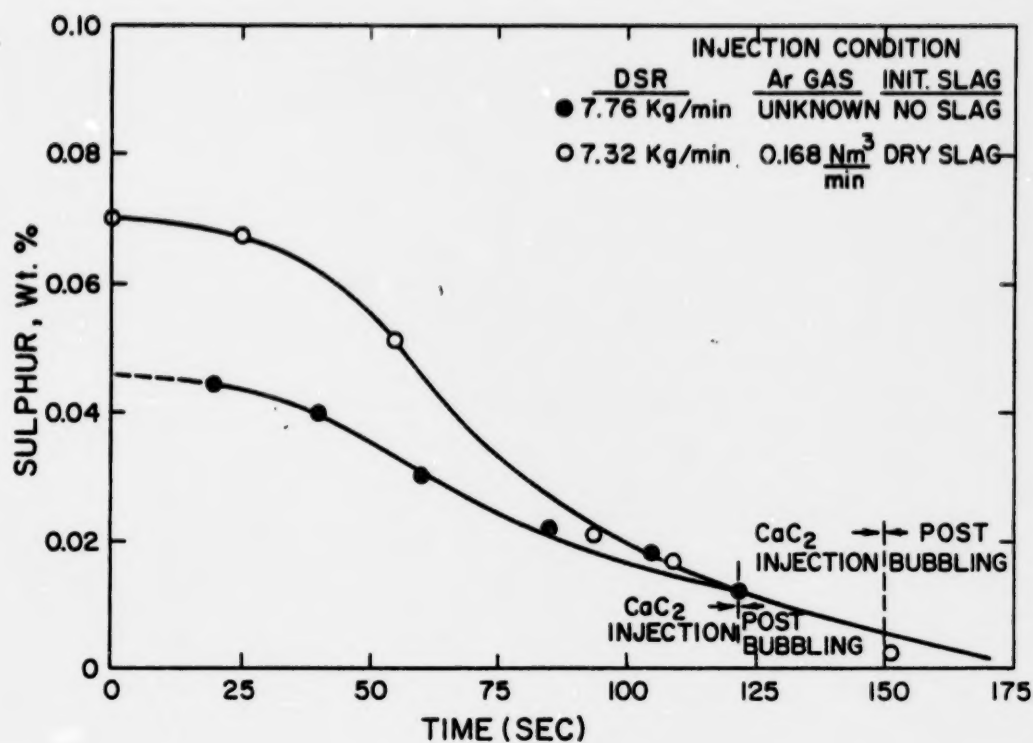


Figure 5: Sulphur versus time for injection H2R2 with no top slag and injection H6R3 with dry slag. Note the incubation time of slow desulphurization.

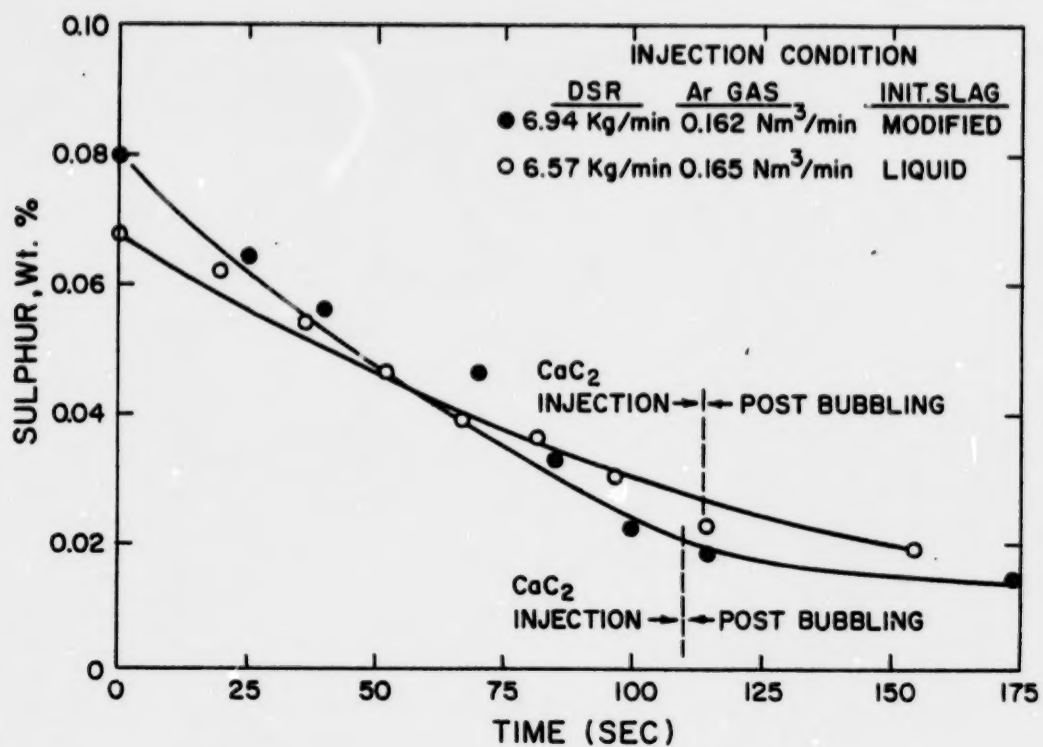


Figure 6: Sulphur versus time for injection H9R3 with liquid top slag and injection H14R2 with aluminum-modified dry slag. Note the absence of an incubation time.

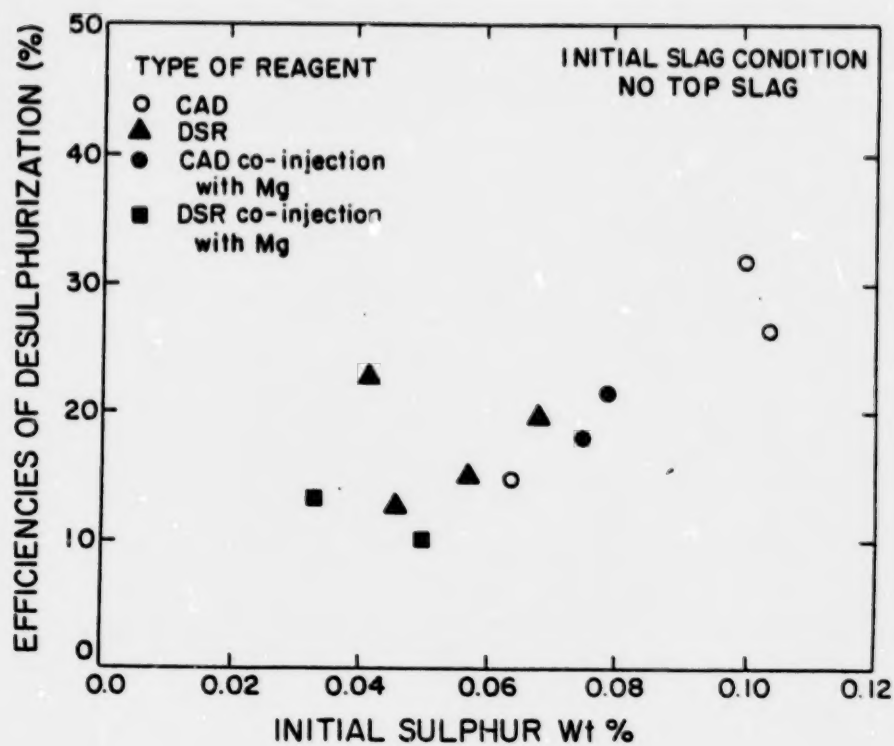


Figure 7: Efficiencies of reagent utilization as a function of initial sulphur content for the runs with no initial top slag.

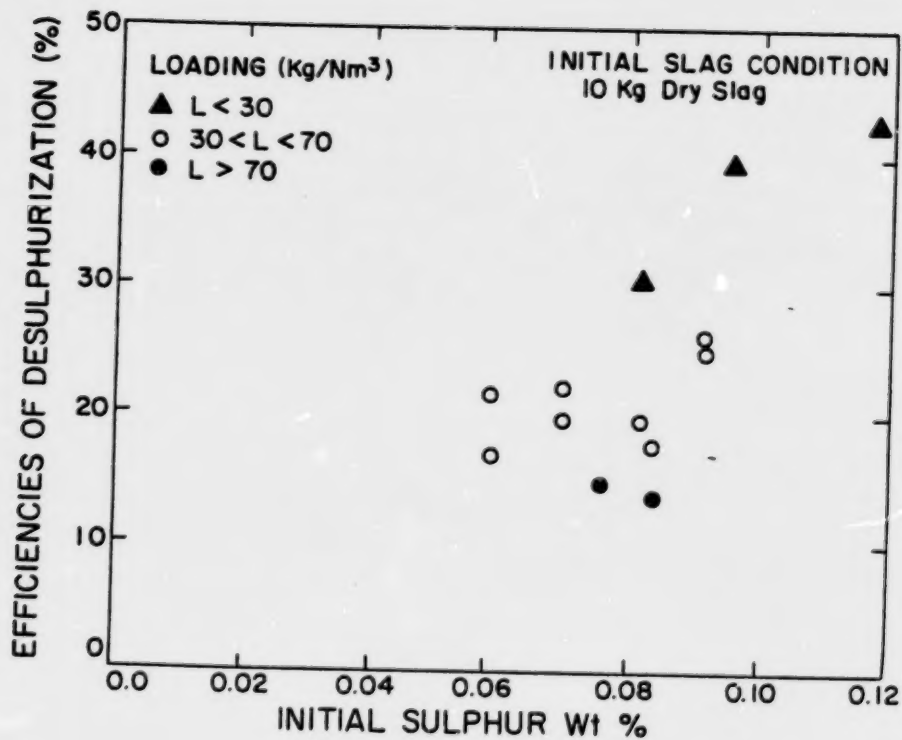


Figure 8: Efficiencies of reagent utilization as a function of initial sulphur content for the runs with dry slags. Loading refers to the ratio of the solid injection rate to the gas flow rate.

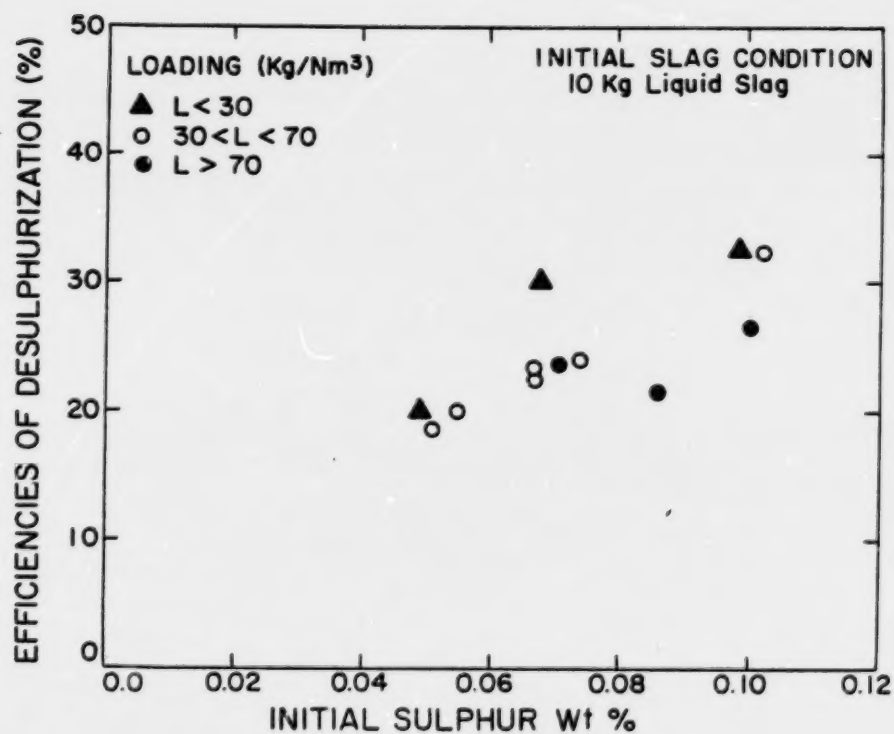


Figure 9: Efficiencies of reagent utilization as a function of initial sulphur content for the runs with liquid slags. Loading refers to the ratio of the solid injection rate to the gas flow rate.

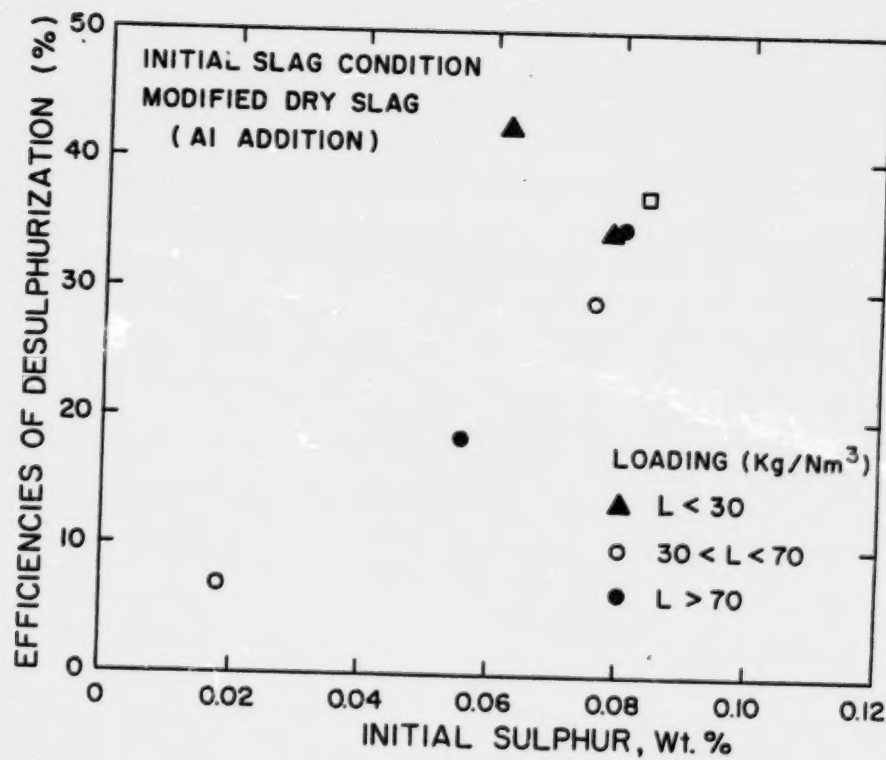


Figure 10: Efficiencies of reagent utilization as a function of initial sulphur content for the runs with dry slags modified with aluminum. Loading refers to the ratio of the solid injection rate to the gas flow rate.

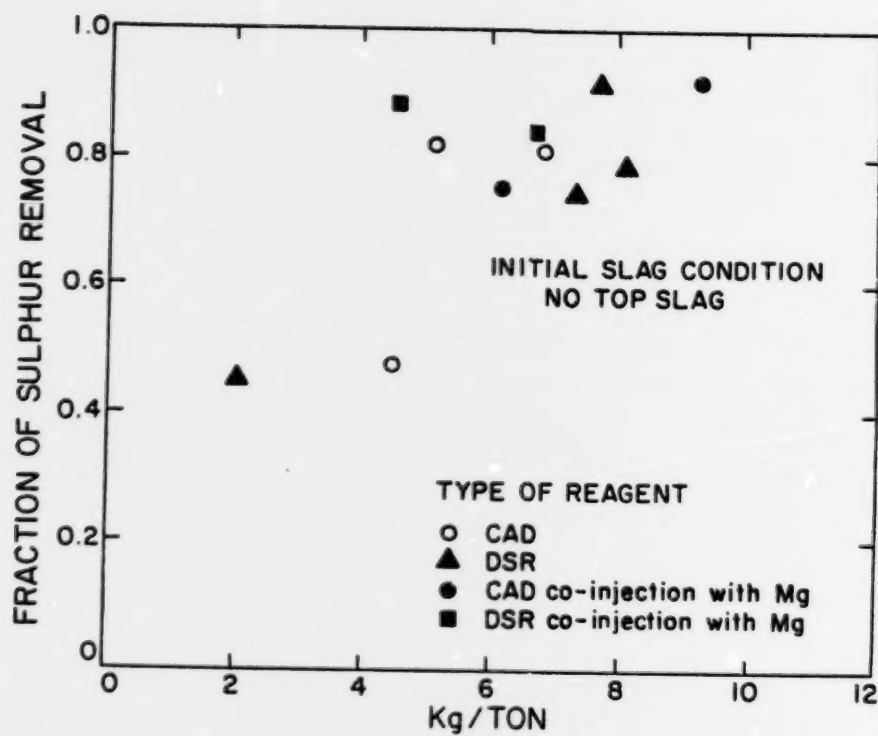


Figure 11: Fraction of the initial sulphur removed as a function of the amount of reagent added for the no slag cases.

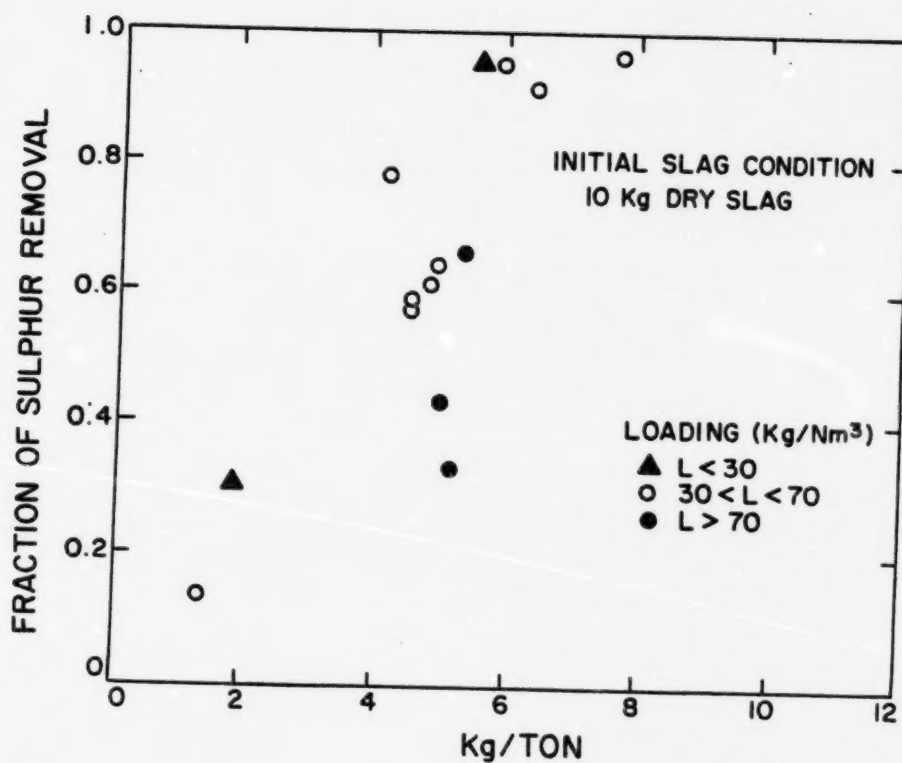


Figure 12: Fraction of the initial sulphur removed as a function of the amount of reagent added to the dry slag cases. Loading refers to the ratio of the solid injection rate to the gas flow rate.

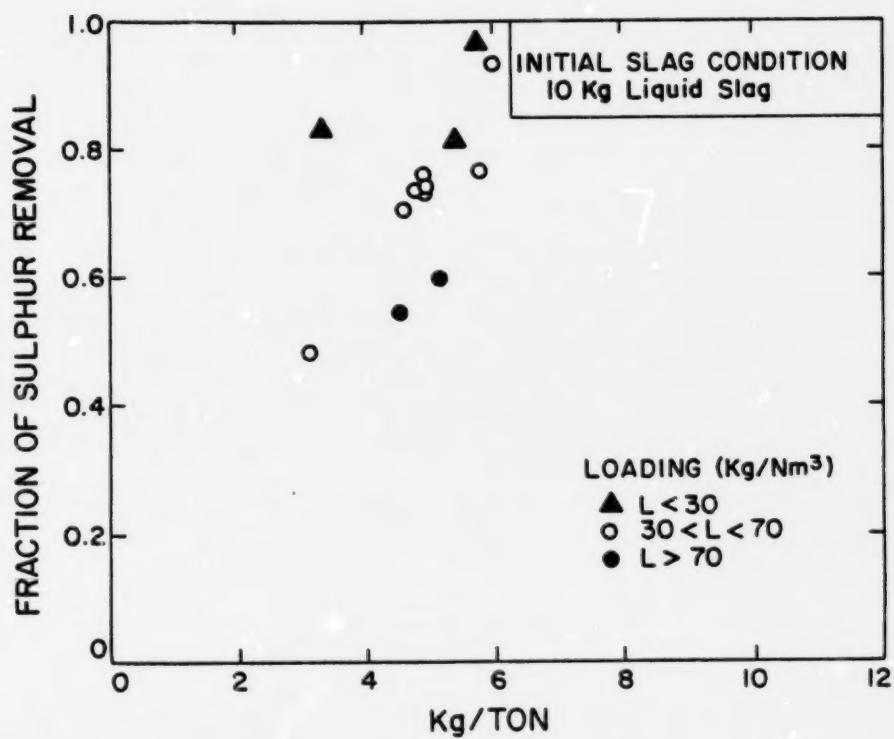


Figure 13: Fraction of the initial sulphur removed as a function of the amount of reagent added for the liquid slag cases. Loading refers to the ratio of the solid injection rate to the gas flow rate.

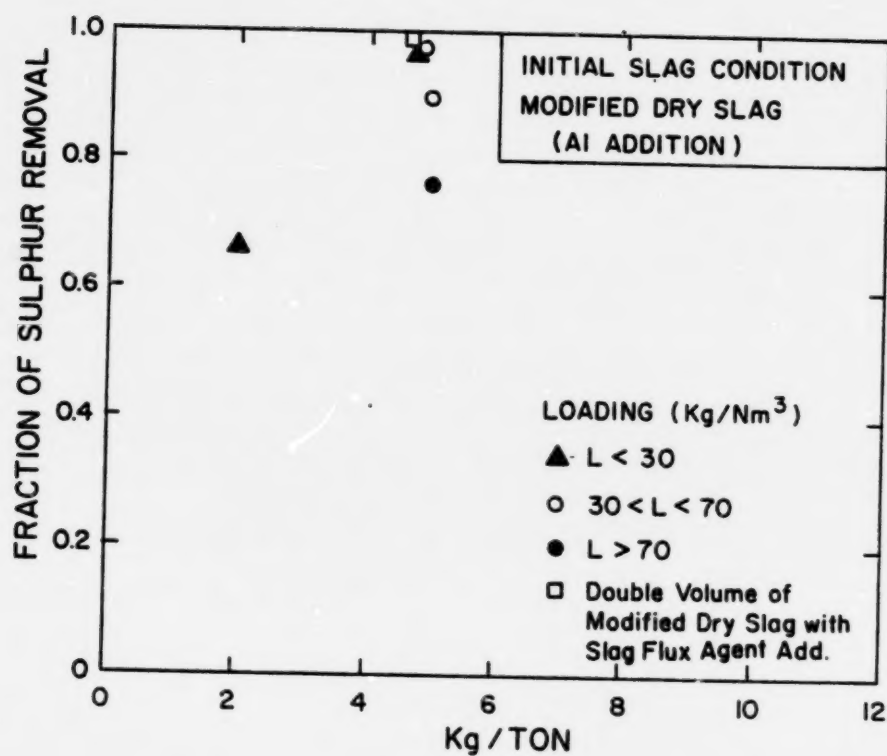


Figure 14: Fraction of the initial sulphur removed as a function of the amount of reagent added for the dry slags modified with aluminum. Loading refers to the ratio of the solid injection rate to the gas flow rate.

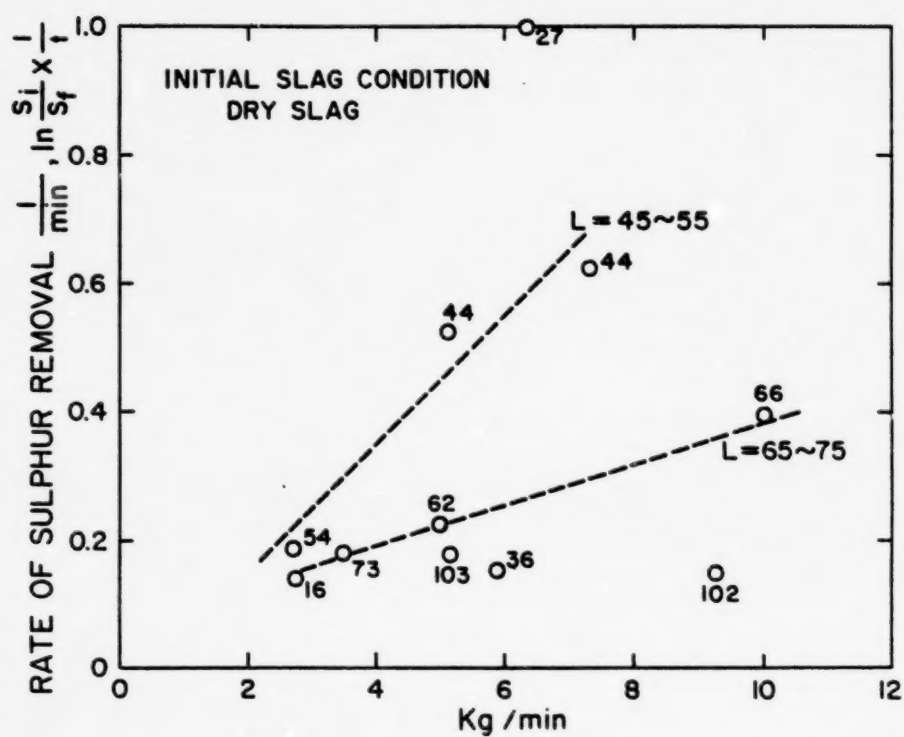


Figure 15: Index of sulphur removal rate as a function of the reagent injection rate for the dry slags. The loadings, L , (kg of reagent/ Nm^3 of argon) are given for each point.

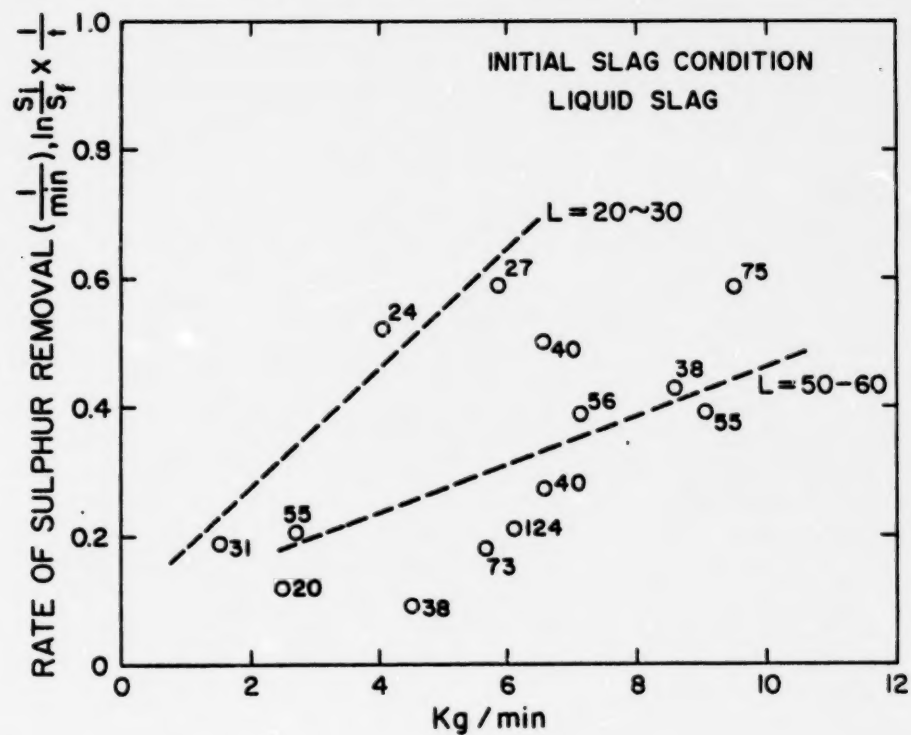


Figure 16: Index of sulphur removal rate as a function of the reagent injection rate for the liquid slags. The loadings, L, (kg of reagent/Nm³ of argon) are given for each point.

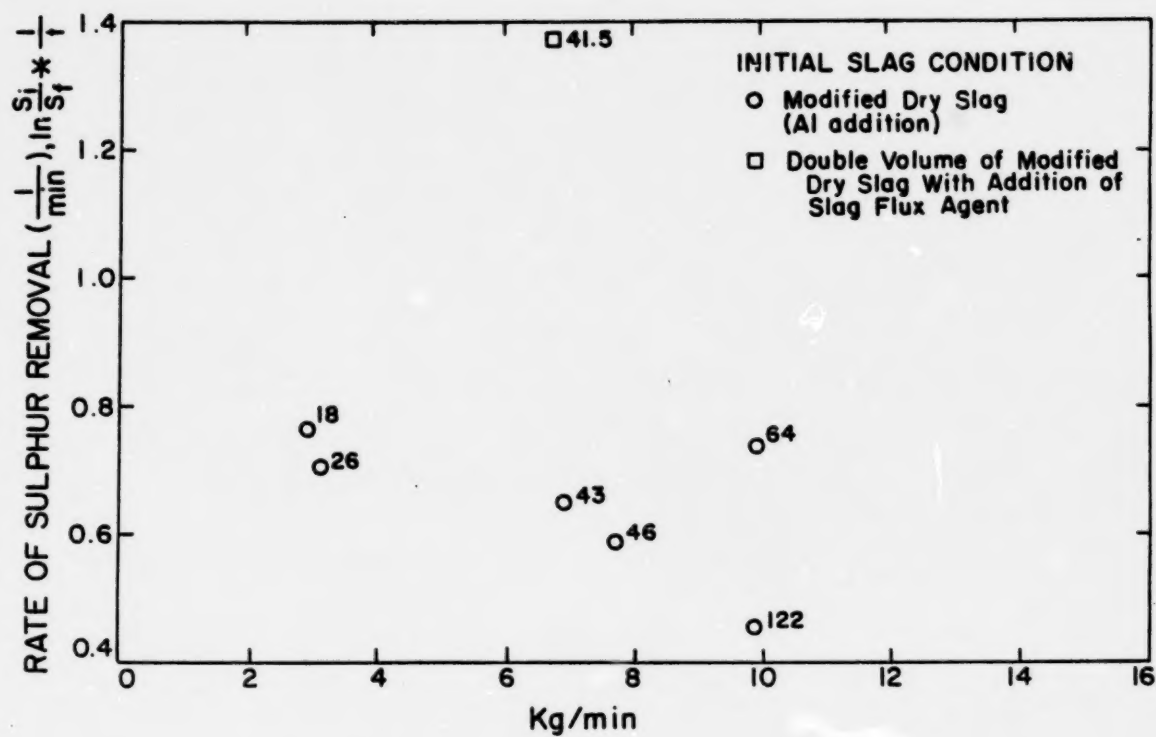


Figure 17: Index of sulphur removal rate as a function of the reagent injection rate for the dry slags modified with aluminum. The loadings, L, (kg of reagent/Nm³ of argon) are given for each point.

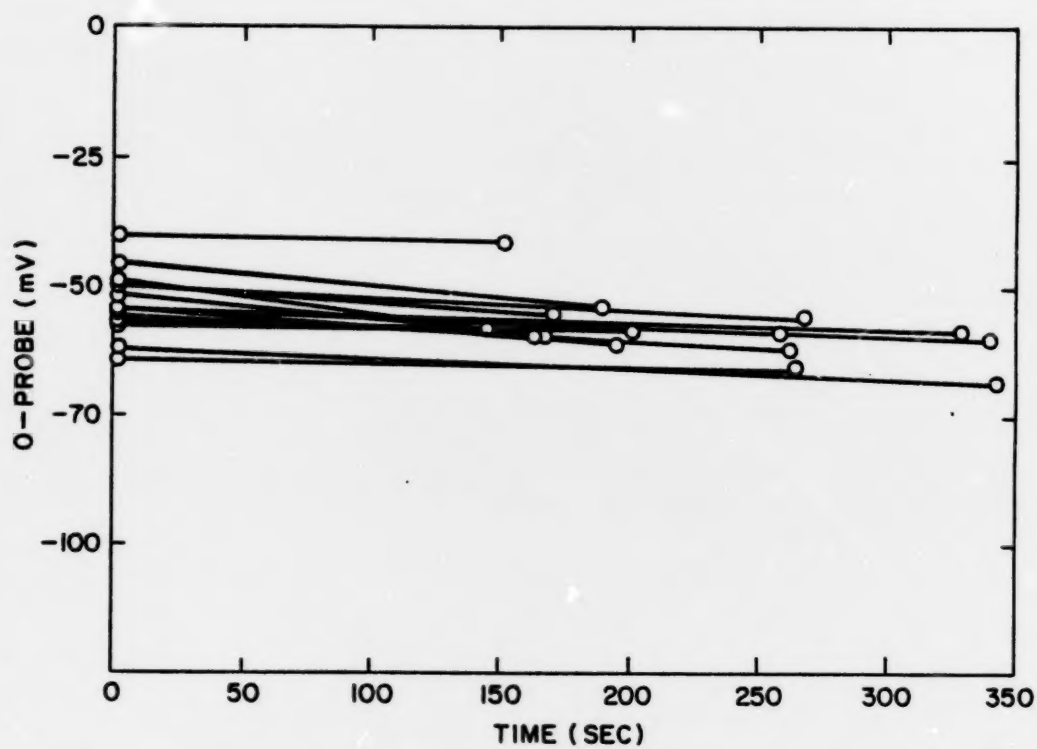


Figure 18: Emf readings from the oxygen probe before and after reagent injection for the cases in which no aluminum was used.

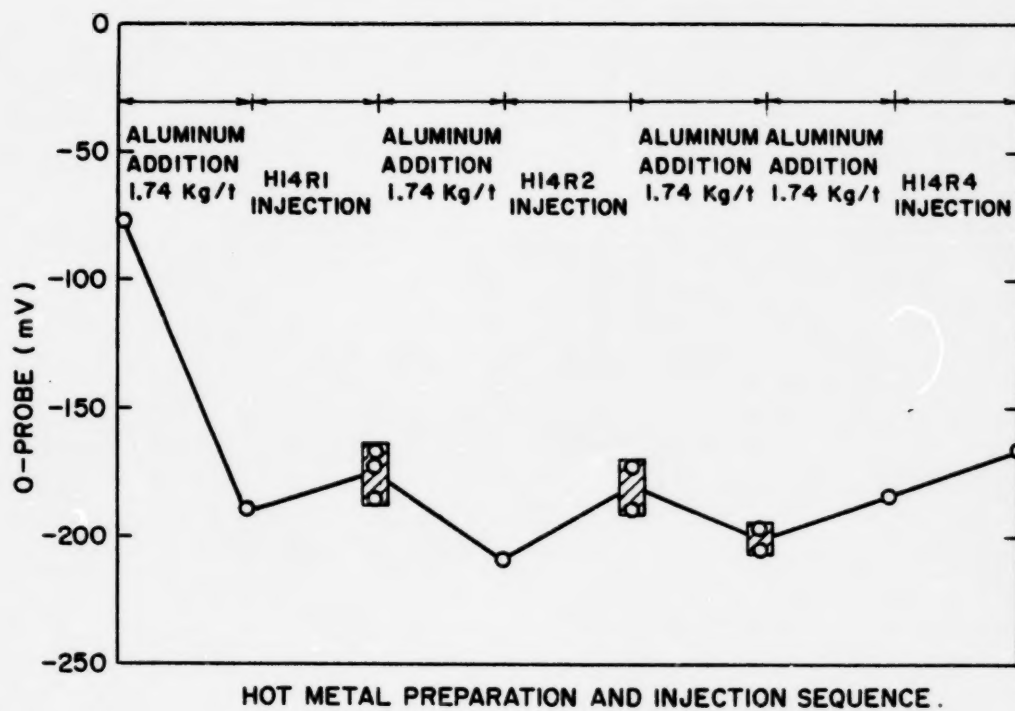


Figure 19: Emf readings from the oxygen probe during heat 14. Note that the aluminum depresses the oxygen, while the holding periods and injection of carbide raises it.

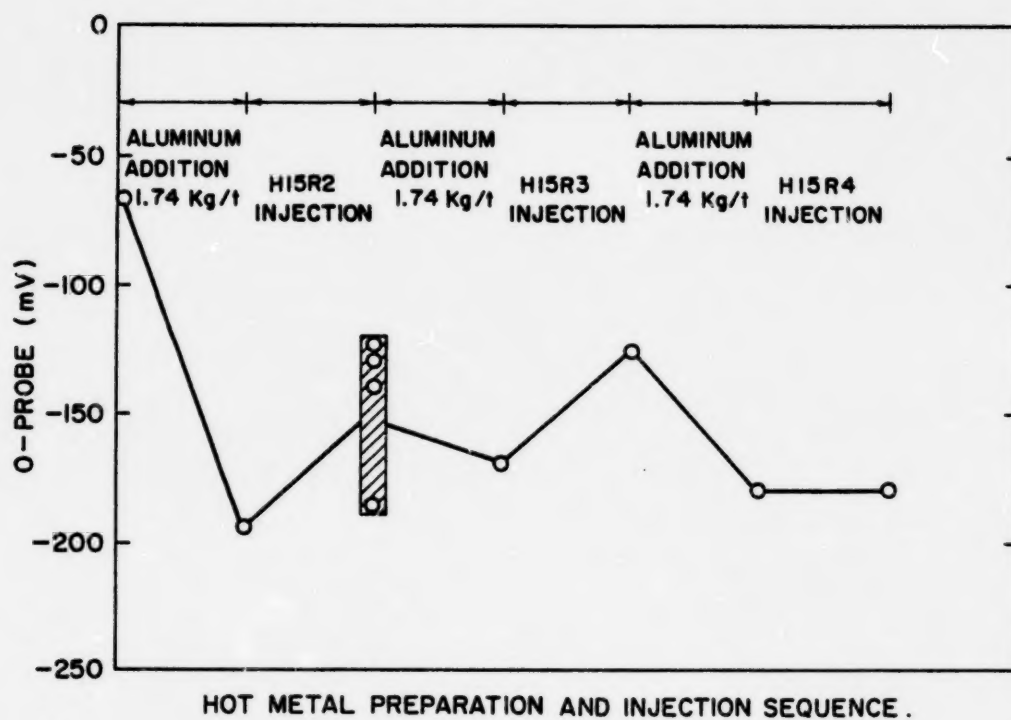


Figure 20: Emf readings from the oxygen probe during heat 15. Note that the aluminum depresses the oxygen, while the holding periods and injection of carbide raises it.

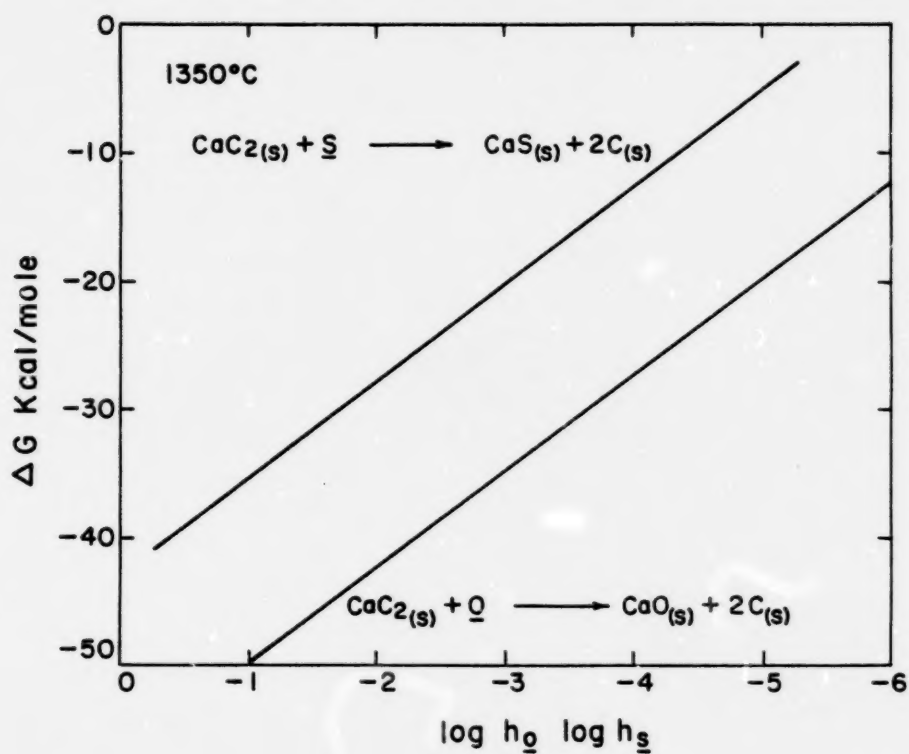


Figure 21: Free energy of reaction of calcium carbide with oxygen and sulphur as a function of Henrian activities of oxygen and sulphur.

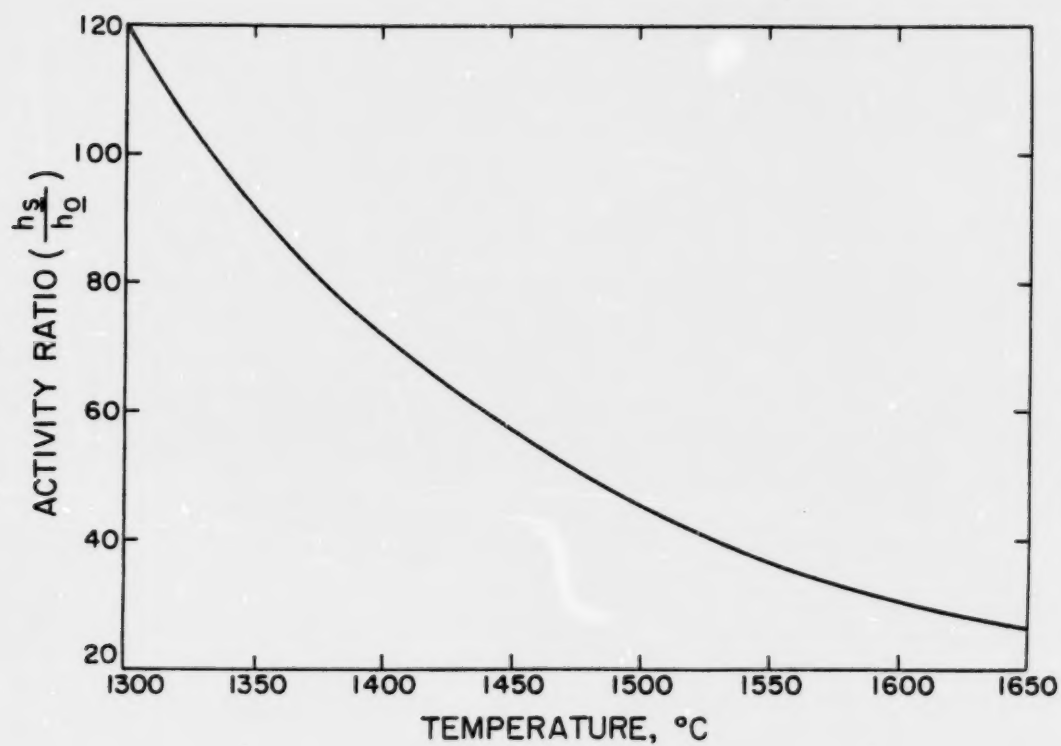


Figure 22: The critical ratio of sulphur and oxygen activities for desulphurization with calcium carbide to proceed as a function of temperature.

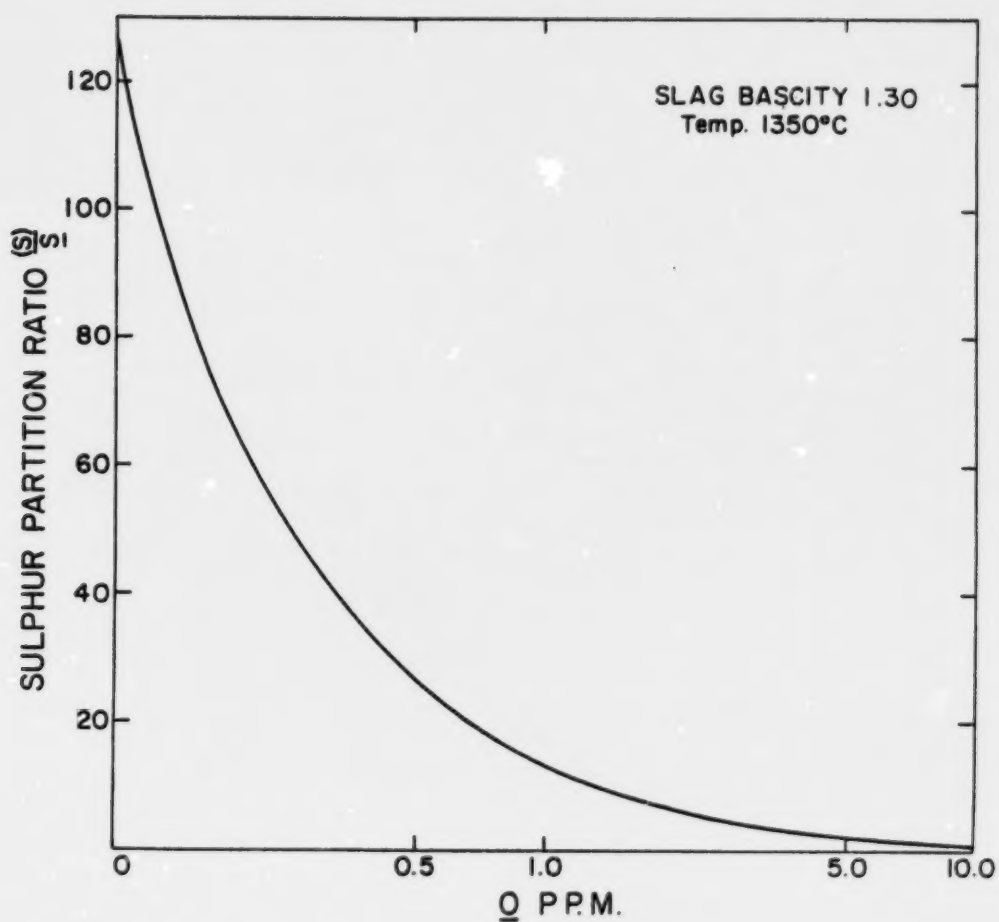


Figure 23: Sulphur partition ratio between slag and metal for slags of 1.3 basicity at 1350°C as a function of the Henrian activity of oxygen.

APPENDIX I

SULPHUR VERSUS TIME CURVES FOR ALL INJECTIONS

